

Cd_{1-x}Hg_xTe (0 ≤ x ≤ 0.5) Thin Films Deposited by a Liquid Phase Chemical Deposition Route

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Abstract: Solar energy utilization will play a vital role in solving the world's energy needs of the future. Fuel transport and storage problems are eliminated in a photovoltaic power system. But the development of the photovoltaic cells, such as silicon, is hampered by the present cost of the materials and fabrication. As an alternative for achieving this solar to electrical conversion, thin film semiconductor / liquid junction systems based on the photo electrochemical effect are of prime importance. The basic materials are cheap and the actual material can easily be obtained from an aqueous alkaline medium (pH=10.5) by deposition of Cd²⁺, Hg²⁺ and Te²⁻ ions. The temperature and time for deposition were optimized as 80 °C and 90 min, 70 ± 2 rpm, and pH equal to 10 ± 0.2 respectively. The layer surface was cleaned after every successive deposition by double distilled water. The deposits were adherent to the substrate support, uniform and smooth with color changing from white to blackish as Hg²⁺ concentration was varied from 0 to 0.5. The electrochemical detector cells were formed out of these series of films as the active photoelectrodes, an electrolyte and a counter electrode and were characterized through their electrical properties. The variation also suggests that the V_{fb} value for a cell with x = 0.1 is approximately 420 mV more negative than that of the CdTe. V_{fb} values for other cell structures are found to increase with Hg concentration up to 0.1 and then decreased on the higher side. These electrochemical detectors exhibited a considerable amount of recombination and series resistance effects.

Keywords: Electrochemical cell, C-V characteristics in dark, flat band potential, photoconductivity etc.

I INTRODUCTION

Solar energy utilization will play a vital role in solving the world's energy needs of the future / 1 /. The direct conversion of sunlight into electricity by solar cells is likely to be a prime method of the future, assuming that practical economic means of direct conversion can be developed. In practice, solar cells have an advantage over the thermal conversion modes in that it responds linearly to the flux. There is no inertia to a solar cell system; it immediately produces its output at the level appropriate to the solar intensity unlike solar thermal systems that need time to reach operating temperature. Fuel transport and storage problems are eliminated in a photovoltaic power system. But the development of the photovoltaic cells, such as silicon, is hampered by the present cost of the materials and fabrication / 1 /. As an alternative for achieving this solar to electrical conversion, thin film semiconductor / liquid junction systems based on the photo electrochemical effect are of prime importance / 2-9 /. These systems possess several advantages over the conventional solid-state solar cells. These are:

1. The junction can be formed very easily and spontaneously ; just on immersion of the semiconductor electrode in a suitable electrolyte.
2. The geometry of the junction is so simple that radiations can impinge directly on the space charge region, minimizing the surface recombination losses, and
3. The most important one is its low production cost and a storage facility. Several reviews on semiconductor / electrolyte interfaces are now available in the literature / 3-7, 9 / and mechanism of the charge transfer across the electrode / electrolyte interface is now fairly understood. For a reasonably efficient conversion of solar energy, several crucial factors are of importance and are studied with respect to the electrode reactions of the semiconductor photoelectrodes. Especially, stabilization of a photoelectrode material with smaller band gap is a main problem and has been partly attended by the redox reactions. The search for easily preparable, highly efficient and stable electrode is essential for low cost energy conversion devices. The better conversion efficiency yield is obtained when the optical gap of the photoelectrode material lies between 1.1 eV - 1.4 eV.

II. EXPERIMENTAL DETAILS

2.1. Preparation of the CdTe and Cd_{1-x}Hg_xTe thin film electrodes

For CdTe films, 10 ml (1M) CdCl₂ solutions was taken in a beaker and 17 ml aqueous ammonia was added to adjust the pH of the reaction mixture (pH = 10 ± 0.2). An appropriate amount of sodium tellurosulphite was then added to the reaction solution and the reaction volume was then made 180 ml by adding distilled water. Thoroughly cleaned glass substrates were rotated in the reaction mixture with a constant speed to yield the quality films. For Cd_{1-x}Hg_xTe films, calculated amount of Hg²⁺ was directly added into the reaction mixture keeping the other conditions the same. The deposition parameters such as temperature, time of deposition and speed of the substrate rotation were kept constant at their optimized values / 10-11 /.

2.2. Fabrication and characterization of the electrode/electrolyte interfaces

The measurements on I-V characteristics in dark were made for all these cells. A

Hewlett-Packard 6,1/2 digit multimeter was used to measure the current flowing through the junction. Under reverse bias condition, the C-V measurements were carried out using three-electrode system. The potential applied across the junction (vs SCE) was varied by a (10 turn, 1 KΩ) helical potentiometer and was measured by an Argonic-113, 4,1/2 digit voltmeter. The junction capacitance was measured using an Aplab-4910, 4,1/2 digit capacitance meter at a superimposed frequency of 1KHz, 1V pp voltage. The barrier height of the various cell configurations were determined by noting the temperature dependent reverse

saturation current of the cells. The current was measured with a nano ammeter, DNM 121, 4-1/2 digit current meter. The temperature of the cell was varied from 30°C to 90°C . The measurements on I-V characteristics in dark were made for all these cells. A Hewlett-Packard 6,1/2 digit multimeter was used to measure the current flowing through the junction. Under reverse bias condition, the C-V measurements were carried out using three-electrode system. The potential applied across the junction (vs SCE) was varied by a (10 turn, 1 K Ω) helical potentiometer and was measured by an Argonic-113, 4,1/2 digit voltmeter. The junction capacitance was measured using an Aplab-4910, 4,1/2 digit capacitance meter at a superimposed frequency of 1KHz, 1V pp voltage. The barrier height of the various cell configurations were determined by noting the temperature dependent reverse saturation current of the cells. The current was measured with a nano ammeter, DNM 121, 4-1/2 digit current meter. The temperature of the cell was varied from 30°C to 90°C

III. RESULT AND DISCUSSION

3.1 The I-V characteristics in dark

The dark I-V characteristics for various cell configurations were studied at room temperature. When a semiconductor electrode was dipped into an electrolyte solution, a small dark voltage, E_d and a dark current, I_d were noticed in all these cases. The generated voltage was having negative polarity towards the semiconductor electrode. The origin of this dark voltage lies in the difference in the two half cell potentials of a cell and can be expressed as / 3-9, 12,13,16,17 /.

$$E_D = E_{\text{CdHgTe}} - E_{\text{graphite}} \quad \dots(1)$$

where E_{CdHgTe} and E_{graphite} are respectively, the equilibrium half cell potentials developed when the CdHgTe and graphite electrodes were dipped into an electrolyte. From the observed polarity it is seen that

$$E_{\text{CdHgTe}} < E_{\text{graphite}} \quad \dots(2)$$

A small dark current generated in the cell suggests that there is some deterioration of the photoelectrode material in the electrolyte solution / 3-9,12-17 /. The electrochemistry and photoelectrochemistry of a semiconductor / electrolyte interface are much complicated compared to the metal / electrolyte interface, however, a simple interpretation of the charge transfer mechanism across the interface is followed assuming the S/E interface as the analog of a Schottky barrier cell for which current through the interface is defined by a well known Butler – Volmer relation as / 13,14,16,17 /

$$I = I_0 \{ \exp [(1-\beta) VF / RT] - \exp (-\beta VF / RT) \} \quad \dots(3)$$

where I_0 is the equilibrium exchange current density, β is the symmetry factor, V is the over voltage, R is the universal gas constant and F is a Faraday constant. A symmetry factor of 0.5 corresponding to a symmetrical barrier yields a symmetrical I versus V curves. This means that the interface cannot rectify the periodically varying potential. When β is taken as $\beta \neq 0.5$, the curves would not be symmetrical and the interface has rectifying properties called as Faradaic rectification / 4-9,16-18 /. The dynamic current voltage relationships were therefore studied in dark at room temperature (300 K) for all the cells under study and few of them are shown in fig.1 as a representative case. The characteristics are non-symmetric in nature. This means that interface has rectification properties and junctions formed are of the rectifying type. The symmetry factor β was therefore calculated for each of the cells from these studies and it was observed that the value of β lies in the range $0.5 < \beta < 0.7$. The I-V characteristics were further analyzed to understand the charge transfer process across the S / E interfaces. The reverse saturation current instead of saturation increased as the reverse voltage was increased. In PEC cells, such kind of behavior is generally observed and is normally due to /4-9,14-17/: i) generation of the electron-hole pairs in the depletion layer under high applied

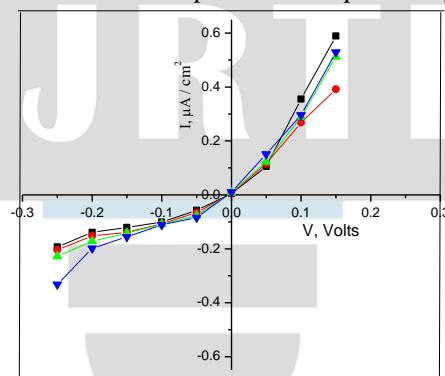


Fig. 1. I-V characteristics in dark for seven representative cells formed with CdHgTe thin film electrodes: a) $x = 0$ (), b) $x = 0.01$ (▲), c) $x = 0.05$ (), d) $x = 0.1$ ().

reverse bias, and ii) onset of the electron – injection from the electrolyte into the semiconductor due to the tunneling process. The junction ideality factors (n_d), which determine the quality of the junction, were determined for all the cells from the log I vs V variations as shown in fig.2. The various n_d values are given in the table 6.2. From the magnitudes of n_d , it is clear that the current transport across the electrode / electrolyte interface has been severely influenced by the cell resistance and recombination mechanism effects due to presence of the surface states and surface adsorbed ions / 4-9,14-17 /.

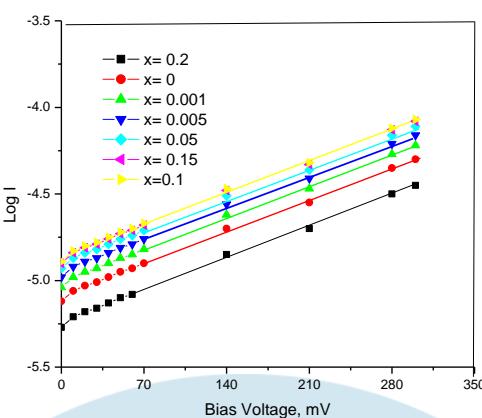


Fig. 2. Plots indicating the variation of $\log I$ vs V for seven representative cells

3.2 The determination of flat band potential

The capacitance voltage (vs SCE) measurements were done on these cells to evaluate the flat band potential (V_{fb}) which determines the relative positions of the Fermi levels of a semiconductor and an electrolyte and consequently the amount of band bending at the interface / 4-9,14,16,17 /. The intrinsic band bending at the interface is a measure of the depletion layer width inside the semiconductor and hence determines ability of the electrode to operate at the short circuit condition. This is also equivalent to a measure of the maximum photo potential (V_{ph}) that can be drawn from a cell. For a semiconductor / electrolyte interface, the observed capacitance is mainly due to the semiconductor space charge region. The capacitances due to the Helmholtz and Gouy diffused layers are assumed negligible owing to the high ionic concentration of the electrolyte / 4-9 /. The space charge capacitance C is related to the applied reverse voltage V as

$$C^{-2} = [2 / (q \epsilon_s \epsilon_0 N_D)] [V - V_{fb} - KT / q] \quad \dots(4)$$

where C is the space charge layer capacitance per unit area, q is the electronic charge, ϵ_s is the semiconductor dielectric constant, ϵ_0 is the permittivity of the free space ($8.86 \times 10^{-12} \text{ F/m}$), V_{fb} is the flat band potential, N_D is the donor density, K is a Boltzman's constant and T is the absolute temperature. The Mott – Schottky (MS) plots were then constructed from the C-V measurements to determine the flat band potentials and are shown in fig. 3.

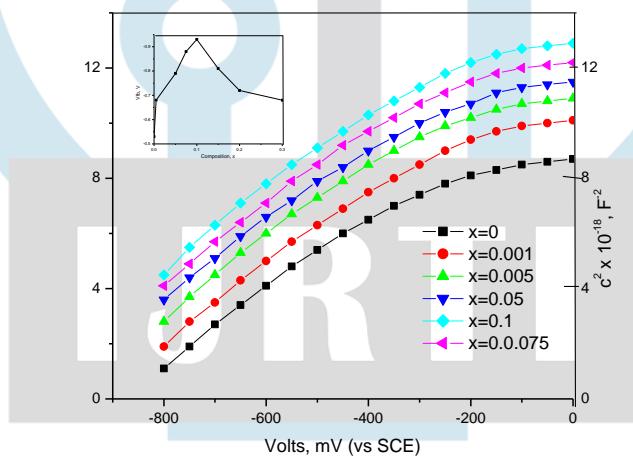


Fig. 3 The M-S plots for typical CdHgTe thin film electrodes with composition

The flat band potentials were then obtained by extrapolating the linear regions of C^{-2} vs V variations on the voltage axis. Variation in the flat band potential with the electrode composition is shown in fig.4 and shows a maximum for a cell formed with photoelectrode of $x = 0.1$ / 10,11 /.

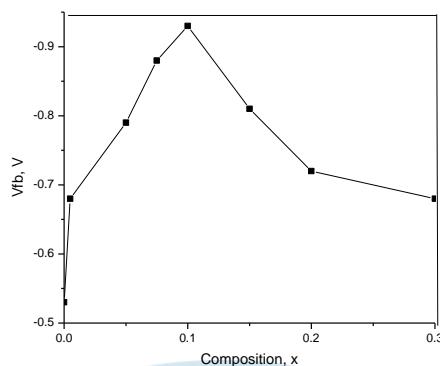


Fig. 4. Variation of the flat band potential (V_{fb}) with the composition parameter, x

The variation also suggests that the V_{fb} value for a cell with $x = 0.1$ is approximately 420 mV more negative than that of the CdTe. V_{fb} values for other cell structures are found to increase with Hg concentration up to 0.1 and then decreased on the higher side / 10,11 /. This change in V_{fb} value with the photoelectrode composition is due to: i) decreased electron affinity as a result of the introduction of Hg^{2+} in CdTe and, ii) increased amount of surface adsorption and band bending at the electrode / electrolyte interface. Where as pinning of Fermi level at higher Hg-contents in the electrode decreases the V_{fb} value / 4-7,10-12,16,17 /.

3.3 Built – in – potential determination

The barrier height also referred as “built – in potential” (ϕ_B 's) was determined for all the cells. The reverse saturation current through the junction at various temperatures from 90 °C down to the room temperature was measured. For a Schottky barrier junction, the reverse saturation current (I_0) is related to the temperature / 4-7,14-16,17,18 / as

$$I_0 = AT^2 \exp(\phi_B / KT) \quad \dots(5)$$

where A and K are the Richardson's and Boltzman constants, respectively and ϕ_B is the barrier height in eV. The reverse saturation current has an exponential dependence on the temperature. Fig.5 shows variation of $\log(I_0 / T^2)$ vs $1000 / T$ for typical cells. ϕ_B 's were then calculated from the linear regions of these plots and are listed in table 1.

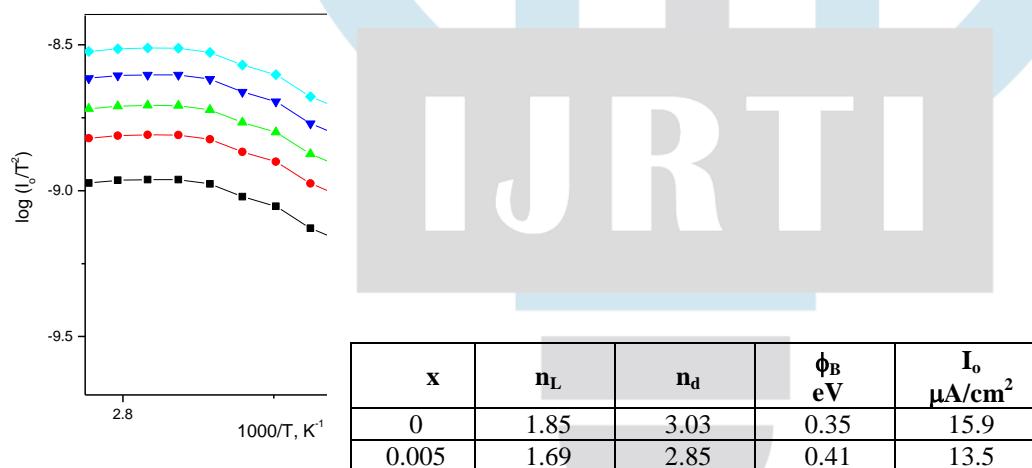


Fig. 5. Variation of $\log I_0 / T^2$ versus $1/T$ for seven representative cells with the photoelectrode composition

Table 1. Various performance parameters of the $Cd_{1-x}Hg_xTe$ thin film based PEC cells.

0.01	1.56	2.50	0.46	12.2
0.05	1.45	2.32	0.53	8.1
0.075	1.35	2.14	0.56	7.4
0.1	1.27	1.96	0.61	5.3
0.15	1.31	2.15	0.58	6.1
0.2	1.4	2.48	0.55	7.5
0.3	1.5	2.54	0.49	8.3
0.5	1.63	2.95	0.43	9.4

3.4 The photoconductivity studies

The room temperature d. c. electrical conductivities in dark (σ_d) for different electrode thicknesses were measured. The conductivities were also measured under constant illumination. For this purpose, the filters of different color's were introduced in the path of the incident light. From these observations, the materials sensitivity,

$$S = (\sigma_L - \sigma_d) / \sigma_d \quad \dots(6)$$

was determined. Fig. 6. shows the variation of materials sensitivity, s with the wavelength of light.

It is observed that the materials sensitivity has been increased with the photoelectrode thickness, which can be ascribed to the increase in crystallite size and decreased intergrannular spacing which in turn decreases the materials resistance.

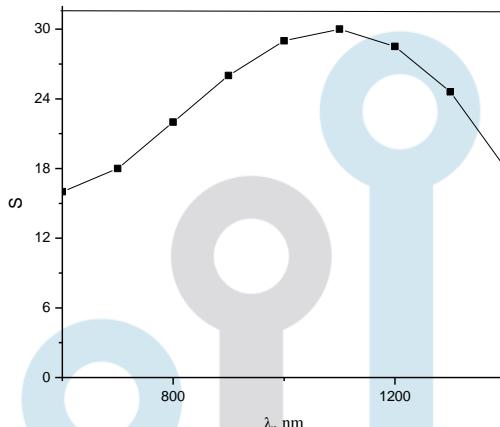


Fig. 6. Spectral Sensitivity S with the wavelength of light.

IV. CONCLUSIONS

The electrochemical photovoltaic cells were formed and the behavior of these cells was examined with a special emphasis given to the photoelectrode composition, x . The dark I-V and C-V characteristics showed presence of the recombination centers surface states at the electrode / electrolyte interface. The PEC cell performance under light excitation is found to be optimum for a cell formed with electrode composition, $x = 0.1$ and is solely due to the increased flat band potential, increased photoelectrode absorption, improved crystalline structure of the photoelectrode material and decreased series resistance of a cell.

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BIOGRAPHY



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